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In re Application of:

Andriessen et al.

Application No. 10/659,982

Filed: September 11, 2003

Art Unit: Unassigned

Examiner: Unassigned

For: PROCESS FOR PREPARING NANO-POROUS METAL OXIDE SEMICONDUCTOR LAYERS

CLAIM OF PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In accordance with the provisions of 35 USC 119, Applicants claim the priority of the following application:

Application No. PCT/EP02/10270, filed in the European Patent Office on September 12, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,

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Date: October 8, 2003

CERTIFICATE OF MAILING

I hereby certify that this CLAIM OF PRIORITY (along with any documents referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Date: 10/8/03 Virginia Scheffke

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Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten internationalen Patentanmeldung überein.

The attached documents are exact copies of the international patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet international spécifiée à la page suivante.

Den Haag, den
The Hague,
La Haye, le
09 SEP 2003

Der Präsident des Europäischen Patentamts
Im Auftrag
For the President of the European Patent Office
Le Président de l'Office européen des brevets
p.o.

C.A.J.A. PASCHE

Patentanmeldung Nr.
Patent application n .
Demande de brev t n° PCT/EP 02/10270

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Demande n°:

PCT/EP 02/10270

Anmelder:
Applicant(s):
Demandeur(s):

1. AGFA - GEVAERT - Mortsel, Belgium

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

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Anmeldetag:
Date of filing:
Date de dépôt:

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PCT/EP 02/10270

PCT REQUEST GN02092

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V	**Designation of States**	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR IE IT LU MC NL PT SE SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT

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V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG UZ VC VN YU ZA ZM ZW	
V-5	**Precautionary Designation Statement** In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	**Exclusion(s) from precautionary designations**	NONE	
VI	**Priority claim**	NONE	
VII-1	**International Searching Authority Chosen**	European Patent Office (EPO) (ISA/EP)	
VIII	**Declarations**	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	**Check list**	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	4	-
IX-2	Description	20	-
IX-3	Claims	2	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	0	-
IX-7	TOTAL	27	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-EASY diskette	-	Diskette

PCT/EP 02/10279

10/09/02 10:30

PROCESS FOR PREPARING NANO-POROUS METAL OXIDE SEMICONDUCTOR LAYERS

Field of the invention

The present invention relates to a process for preparing nano-porous metal oxide semiconductor layers.

Background of the invention.

There are two basic types of photoelectrochemical photovoltaic cells. The first type is the regenerative cell which converts light to electrical power leaving no net chemical change behind. Photons of energy exceeding that of the band gap generate electron-hole pairs, which are separated by the electrical field present in the space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface where they are scavenged by the reduced form of the redox relay molecular (R), oxidizing it: $h^{+} + R \rightarrow O$, the oxidized form. O is reduced back to R by the electrons that re-enter the cell from the external circuit. In the second type, photosynthetic cells, operate on a similar principle except that there are two redox systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In such cells water is typically oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. Titanium dioxide has been the favoured semiconductor for these studies.

Mesoscopic or nano-porous semiconductor materials, minutely structured materials with an enormous internal surface area, have been developed for the first type of cell to improve the light capturing efficiency by increasing the area upon which the spectrally sensitizing species could adsorb. Arrays of nano-crystals of oxides such as TiO_2, ZnO, SnO_2 and Nb_2O_5 or chalcogenides such as CdSe are the preferred semiconductor materials and are interconnected to allow electrical conduction to take place. A wet type solar cell having a porous film of dye-sensitized titanium dioxide semiconductor particles as a work electrode was expected to surpass an amorphous silicon solar cell in conversion efficiency and cost. These fundamental techniques were disclosed in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740 and in US 4,927,721, US 5,350,644 and JP-A 05-504023. Graetzel et al

reported solid-state dye-sensitized mesoporous TiO_2 solar cells with up to 33% photon to electron conversion efficiences.

In 1995 Tennakone et al. in Semiconductor Sci. Technol., volume 10, page 1689 and O'Regan et al. in Chem. Mater., volume 7, page 1349 reported an all-solid-state solar cell consisting of a highly structured hetero-junction between a p- and n-type semiconductor with a absorber in between in which the p-semiconductor is CuSCN or CuI, the n-semiconductor is nano-porous titanium dioxide and the absorber is an organic dye.

EP-A 1 176 646 discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that if further comprises a sensitizing semiconductor, said sensitizing being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovolaic cell.

A drawback in the manufacture of nano-porous metal oxide semiconductor layers for Graetzel photovoltaic cells is the high temperature needed for making the nano-porous metal oxide semiconductor layer. This is apparently needed to obtain sufficient contact between the nano-porous metal oxide particles to create a conductive pathway for the photogenerated charges (electrons). Although the term sintering is not the appropriate one in this context, this term is often used to describe this heating process. Usually temperatures between 300 and 550°C are applied for 15 to 90 minutes. Such high temperatures are prohibitive for making photovoltaic cells on plastic and flexible substrates. Such cells would offer a myriad of advantages for this type of photovoltaic cell.

WO 00/72373 discloses a method for manufacturing a nanostructured porous film electrode, the method characterized by the steps of: preparing a binder-free suspension (21) of electrode material particles (11) in a volatile suspending agent (13), said particles substantially having a size within the nanometer scale, depositing the binder-free particle suspension (21) on a substrate (22) covered with a conducting film, removing the suspending agent (31) by evaporation, and compressing the particles to form an electrically conducting and mechanically stable nanostructured porous film. The process of WO 00/72373 enables the realization of the same solar cell performance with high pressure sintered nano-porous titanium dioxide layers as with conventional high temperature sintering. This finding was confirmed in 2000 by Pichot et al. in Langmuir, volume 16, pages 5625 to 5630, and in

2001 by Lindstrom et al. in Nano Letters, volume 1, pages 97 to 100. However, although this high pressure sintering process appears to work quite well with Degussa P25, a nano-sized titanium dioxide with a mean particle size of 30 nm and a specific surface of 50 m^2/g from DEGUSSA, on a glass substrate or a plastic substrate, it has been found not to work with titanium dioxide particles made by a wet precipitation process.

There is a therefore a need for a low temperature process for preparing nano-porous metal oxide semiconductor layers with nano-particles prepared by wet precipitation processes on supports.

Aspects of the invention.

It is therefore an aspect of the present invention to provide a process for preparing nano-porous metal oxide semiconductor layers with nano-particles prepared by a wet precipitation process on both flexible and rigid supports.

It is a further aspect of the present invention to provide a photovoltaic cell incorporating a nano-porous metal oxide semiconductor layer prepared with nano-particles prepared by a wet precipitation process on flexible and rigid supports.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention.

It has been surprisingly found that layers of nano-porous metal oxide semiconductors can be prepared with nano-particles prepared by a wet precipitation process on supports by a process involving preheating the nano-particles at a temperature of 250 to 600°C, applying a coating of these preheated nano-particles to the support and subjecting the coating to a pressure of 100 to 1000 bar, without the application of the high temperatures needed for conventional sintering of titanium dioxide nano-particles i.e. 300 to 550°C.

Aspects of the present invention are realized by a process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of the heat-treated nano-particles from step (ii), (iv) applying the dispersion of step

(iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature below 250°C. An electrically conducting and mechanically stable nano-porous metal oxide semiconductor layer is thereby prepared.

Aspects of the present invention are also realized by a layer of a nano-porous metal oxide semiconductor obtainable by the above-mentioned process.

Aspects of the present invention are also realized by a photovoltaic device comprising a layer of a nano-porous metal oxide semiconductor obtainable by the above-mentioned process.

Preferred embodiments are disclosed in the dependent claims.

Detailed description of the invention.

Definitions

The term nano-porous metal oxide semiconductor means a metal oxide semiconductor having pores with a size of 100 nm or less and having an internal surface area of at least 5 m^2/g and not more than 300 m^2/g.

The term chalcogenide means a binary compound containing a chalcogen and a more electropositive element or radical. A chalcogen is an element from group IV of the periodic table including oxygen, sulphur, selenium, tellurium and polonium.

The term "support" means a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in direct contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

The term coating is used as a generic term including all means of applying a layer including all techniques for producing continuous layers, such as curtain coating, doctor-blade coating etc., and all techniques for producing non-continuous layers such as screen printing, ink jet printing, flexographic printing, and techniques for producing continuous layers.

The abbreviation PEDOT represents poly(3,4-ethylenedioxy-thiophene).

The abbreviation PSS represents poly(styrene sulphonic acid) or poly(styrenesulphonate).

Process for preparing a layer of a nano-porous metal oxide semiconductor

Aspects of the present invention are realized by a process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of the heat-treated nano-particles from step (ii), (iv) applying the dispersion of step (iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature below 250°C.

According to a first embodiment of the process, according to the present invention, the metal oxide semiconductor is n-type.

According to a second embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor has a band-gap of greater than 2.9 eV.

According to a third embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor nano-particle have a mean number averaged particle size ≤ 20 nm.

According to a fourth embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

According to a fifth embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor is titanium dioxide.

According to a sixth embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor is titanium dioxide and between 80 and 100% thereof has an anatase morphology.

According to a seventh embodiment of the process, according to the present invention, the nano-porous metal oxide semiconductor is titanium dioxide and between 90 and 100% thereof has an anatase morphology.

According to an eighth embodiment of the process, according to the present invention, the pretreatment temperature is in the range of 300 to 500°C.

According to a ninth embodiment of the process, according to the present invention, the pretreatment temperature is in the range of 350 to 450°C.

According to a tenth embodiment of the process, according to the present invention, the sintering pressure is in the range of 300 to 700 bar. According to an eleventh embodiment of the process, according to the present invention, the sintering pressure is in the range of 400 to 600 bar.

According to a twelfth embodiment of the process, according to the present invention, the process further comprises heating the coating subjected to pressure from step (v) at a temperature of 100 to 200°C. According to a thirteenth embodiment of the process, according to the present invention, the process further comprises heating the coating subjected to pressure from step (v) at a temperature of 125 to 170°C.

According to a fourteenth embodiment of the process, according to the present invention, step (v) is carried out at a temperature above 0°C.

Step (ii) of the process, according to the present invention, is carried out under the atmosphere and pressure necessary to obtain metal oxide nano-particles with semiconducting properties. According to a fifteenth embodiment of the process, according to the present invention, step (ii) is carried out at under an ambient atmosphere i.e. at the pertaining ambient pressure and under the pertaining ambient atmosphere.

The sintering pressure for a particular layer of a nano-porous metal oxide semiconductor is dependent upon the nature of the support, a sintering pressure of 300 to 700 bar being suitable for glass supports and sintering pressures up to 1000 bar being suitable for polymeric film supports.

For efficient solar cells, the coating of the nano-porous TiO2 should be between 8 and 12 µm in order to have sufficient light absorption for generating power conversion efficiencies up to 5 to 8%. The thicker the titanium dioxide coating, the longer the pathway for the charges (electrons) have to be transported to the charge collecting electrode and the greater the probability of recombination occurring with resultant power conversion efficiency loss. In order to circumvent this problem smaller titanium dioxide nano-particles can be used, having a larger specific surface and

hence enabling thinner layers to be realized with the same light absorbance values. In this way, photovoltaic cells with higher efficiencies can be obtained due to the fact that the probability of recombination is reduced due to the path traversed by the electrons to the charge collecting electrode being shorter.

Step (i) of the process, according to the present invention, provides metal oxide semiconductor nano-particles prepared by a wet precipitation process. The expression "wet precipitation process" distinguishes the metal oxide semiconductor nano-particles used in the process, according to the present invention, from those prepared by non-wet chemical processes such as flame pyrolysis processes such as that operated by Degussa. Suitable titanium dioxide nano-particles produced by wet precipitation processes include:

Ti-Nanoxide™ T	=	a nano-sized anatase titanium dioxide with a mean particle size of 13 nm and a specific surface of 120 m^2/g from SOLARONIX SA;
Ti-Nanoxide™ HT	=	a nano-sized anatase titanium dioxide with a mean particle size 9 nm and specific surface of 165 m^2/g from SOLARONIX SA;

which are often used as n-type semi-conductor nano-particles in making Graetzel-type photovoltaic cells, but can be also readily synthesized using fairly straightforward precipitation techniques familiar in colloid chemistry, such as described, for example, in 1997 by Barbe et al in Journal of the American Ceramic Society, volume 80(12), pages 3157 - 3171, herein incorporated by reference.

Spectral sensitization of nano-porous metal oxide semiconductor layers

Aspects of the present invention are also realized by a layer of a nano-porous metal oxide semiconductor obtainable by a process, according to the present invention.

According to a first embodiment of the layer, according to the present invention, the layer contains at least one spectral sensitizer for the nano-porous metal oxide semiconductor selected from the group consisting of metal chalcogenide nano-particles with a band-gap between 1.5 and 2.9 eV, organic dyes, and metallo-organic dyes.

According to a second embodiment of the layer, according to the present invention, the layer contains at least one spectral sensitizer for the nano-porous metal oxide semiconductor selected from the group consisting of metal oxides, metal sulphides and metal selenides.

According to a third embodiment of the layer, according to the present invention, the layer contains at least one spectral sensitizer for the nano-porous metal oxide semiconductor which is a metal sulphide.

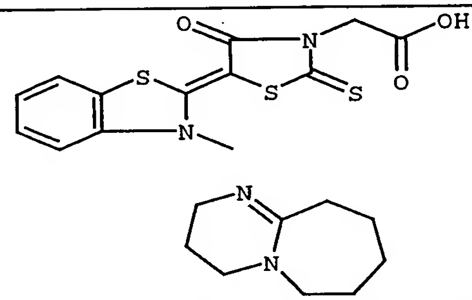
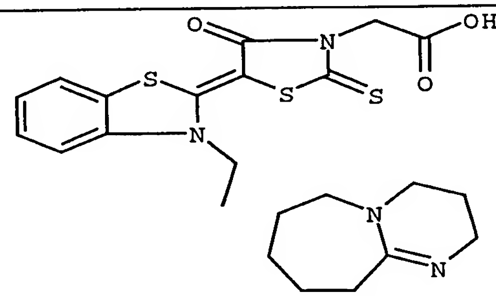
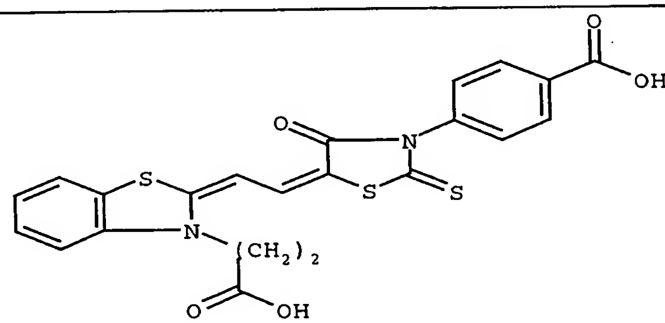
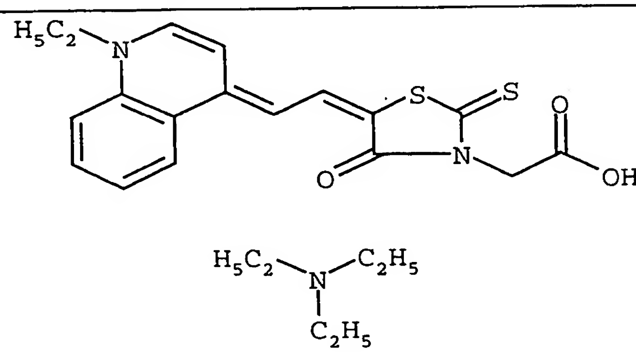
According to a fourth embodiment of the layer, according to the present invention, the layer contains at least one spectral sensitizer for the nano-porous metal oxide semiconductor selected from the group consisting of lead sulphide, bismuth sulphide, cadmium sulphide, silver sulphide, antimony sulphide, indium sulphide, copper sulphide, cadmium selenide, copper selenide, indium selenide, cadmium telluride or a mixture of two or more thereof.

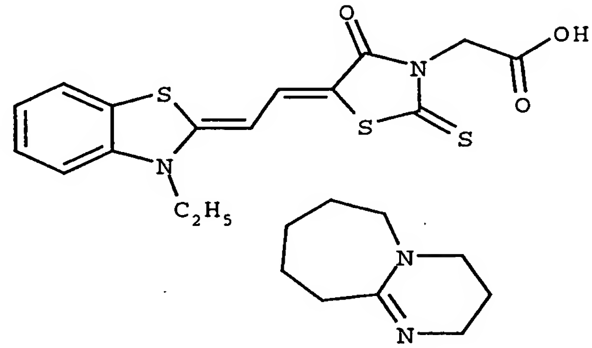
Vogel et al. in 1990 in Chemical Physics Letters, volume 174, page 241, herein incorporated by reference, reported the sensitization of highly porous TiO_2 with in-situ prepared quantum size CdS particles (40-200Å), a photovoltage of 400 mV being achieved with visible light and high photon to current efficiences of greater than 70% being achieved at 400 nm and an energy conversion efficiency of 6.0% under monochromatic illumination with λ = 460 nm. In 1994 Hoyer et al. reported in Applied Physics, volume 66, page 349, that the inner surface of a porous titanium dioxide film could be homogeneously covered with isolated quantum dots and Vogel et al. reported in Journal of Physical Chemistry, volume 98, pages 3183-3188, herein incorporated by reference, the sensitization of various nanoporous wide-bandgap semiconductors, specifically TiO_2, Nb_2O_5, Ta_2O_5, SnO_2 and ZnO, with quantum-sized PbS, CdS, Ag_2S, Sb_2S_3 and Bi_2S_3 and the use of quantum dot-sensitzed oxide semiconductors in liquid junction cells. The internal photocurrent quantum yield decreased with increasing particle diameter and decreased in the order TiO_2 > ZnO > Nb_2O_5 > SnO_2 > Ta_2O_5.

EP-A 1 176 646, herein incorporated by reference, discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that if further comprises a sensitizing semiconductor, said sensitizing being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovolaic cell.

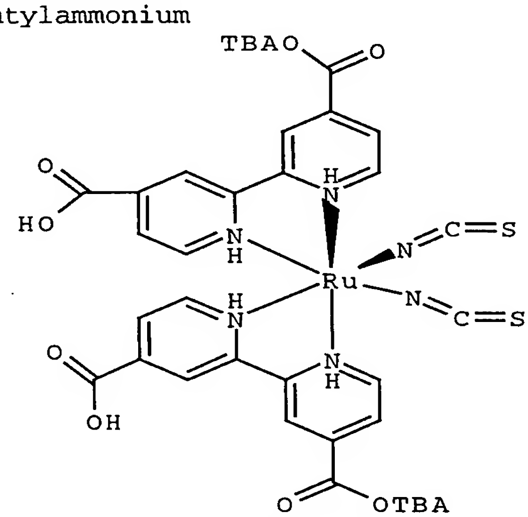
In a preferred embodiment the sensitizing semiconductor is in the form of particles adsorbed at the surface of said electron conductor and in a further preferred embodiment the sensitizing semiconductor is in the form of quantum dots, which according to a particularly preferred embodiment are particles consisting of PbS, CdS, Bi_2S_3, Sb_2S_3, Ag_2S, InAs, CdTe, CdSe or HgTe or solid solutions of HgTe/CdTe or HgSe/CdSe.

Suitable spectrally sensitizing organic dyes (SSOD) include cyanine, merocyanine and anionic dyes, such as:

SSOD-01	
SSOD-02	
SSOD-03	
SSOD-04	

SSOD-05	

Suitable spectrally sensitizing metallo-organic dyes allowing for broad absorption of the solar spectrum include:

	chemical name
Ruthenium 470, a ruthenium dye from Solaronix	tris(2,2'bipyridyl-4,4' dicarboxylato) ruthenium (II) dichloride
Ruthenium 505, a ruthenium dye from Solaronix	cis-bis(isocyanato) (2,2'bipyridyl-4,4' dicarboxylato) ruthenium (II)
Ruthenium 535, a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)
Ruthenium 535 bis-TBA, a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium 
Ruthenium 620 "Black Dye", a ruthenium dye from Solaronix	(anion only) tris(isothiocyanato)-ruthenium(II)-2,2':6',2"-terpyridine-4,4',4"-tricarboxylic acid

Support

Supports for use according to the present invention include polymeric films, silicon, ceramics, oxides, glass, polymeric film

reinforced glass, glass/plastic laminates, metal/plastic laminates, paper and laminated paper, optionally treated, provided with a subbing layer or other adhesion promoting means to aid adhesion to the layer configuration, according to the present invention. Suitable polymeric films are poly(ethylene terephthalate), poly(ethylene naphthalate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulosetriacetate, polyolefins and poly(vinyl chloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

Photovoltaic devices

Aspects of the present invention are realized by a photovoltaic device comprising a layer of a nano-porous metal oxide semiconductor obtainable by a process, according to the present invention.

Photovoltaic devices comprising a layer of a nano-porous metal oxide semiconductor prepared by a process, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of photovoltaic cell, as exemplified by the Graetzel cell, the hole transporting medium may be a liquid electrolyte supporting a redox reaction, a gel electrolyte supporting a redox reaction, an organic hole transporting material, which may be a low molecular weight material such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (OMeTAD) or triphenylamine compounds or a polymer such as PPV-derivatives, poly(N-vinylcarbazole) etc., or inorganic semiconductors such as CuI, CuSCN etc. The charge transporting process can be ionic, as for example in the case of a liquid electrolyte or gel electrolyte or electronic, as for example in the case of organic or inorganic hole transporting materials.

Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer, an adhesive etc. to prevent deterioration or volatilization of the inside substances. The external circuit connected to the electrically-conductive substrate and the counter electrode via the respective leads is well-known.

Alternatively the layer of a nano-porous metal oxide semiconductor prepared by a process, according to the present invention, can be incorporated in hybrid photovoltaic compositions such as described in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740, in 1998 by U. Bach et al. [see Nature, volume 395, pages 583-585 (1998)] and in 2002 by W. U. Huynh et al. [see Science, volume 295, pages 2425-2427 (2002)].

Industrial application

Layers of nano-porous metal oxide semiconductors prepared according the process, according to the present invention, can be used in both regenerative and photosynthetic photovoltaic devices.

The invention is illustrated hereinafter by way of reference and invention photovoltaic devices. The percentages and ratios given in these examples are by weight unless otherwise indicated.

EXAMPLE 1

Preparation of Titanium dioxide nano dispersions

Dispersion 1:

P25 a nano-sized titanium dioxide with a mean particle size of 25 nm and a specific surface of 55 m^2/g from DEGUSSA was mixed with ethanol to give a 25% by weight of solid material and then treated ultrasonically to produce Dispersion 1.

Dispersion 2:

285 g of Ti-isopropoxide, 1800 mL of deionized water and 12.5 mL of nitric acid were stirred overnight at 80°C without a cover. The total volume was made up to 1400 mL with deionized water and then autoclaved at 230°C for 14 hours. The concentration of the autoclaved colloid was reduced by evaporation to 16.2% by weight of solid material and then sufficient ethanol added to give a final solids content of 10.8% by weight, thereby producing Dispersion 2 (mean particle size of 13 nm, specific surface area 120 m^2/g).

Dispersion 3:

Ti-Nanoxide™ T from SOLARONIX, having a mean particle size of 13 nm, a specific surface of 120 m2/g and containing 11% by weight of titanium oxide is called dispersion 3.

Heat pretreatment of the Titanium dioxide nano dispersions

Dispersions 2 or 3 were dried in a rotary evaporator, ground, spread on a sheet of glass and heated at 200, 350, 400 or 450°C, depending on the experiment, for 30 minutes in a rotary tube furnace. The resulting powders were then cooled, ground again and converted into a paste by adding water, ethanol and 10-20 µL of nitric acid. To prevent material loss, the paste was diluted with water and put in a bottle. The excess liquid was evaporated at a temperature of 100-150°C prior to use.

Evaluation in photovoltaic devices with liquid electrolyte

Photovoltaic devices 1-46 were prepared by the following procedure:

Preparation of the front electrode:

A glass plate (2 x 7 cm^2) coated with conductive SnO_2:F (Pilkington TEC15/3) with a surface conductivity of ca 15 Ohm/square was ultrasonically cleaned in isopropanol for 5 minutes and then dried. The electrode was taped off at the borders and was doctor blade-coated in the middle (0.7 x 4.5 cm^2) with the titanium dioxide colloidal dispersion with or without dilution with ethanol depending upon the desired layer thickness.

The layer thickness was determined mechanically with a diamond-tipped probe (Perthometer) and interferometry and are given in Tables 1 to 4.

i) *Front electrodes prepared by high temperature sintering of nano-porous titanium dioxide layers:*

Coated glass electrodes with the nano titanium dioxide dispersions were heated at 450°C for 30 minutes, then cooled to 150°C by placing it on a hot plate at 150°C for 10 minutes, then immediately immersed in a 2 x 10^{-4} M solution of the Ruthenium 535 dye (SOLARONIX) for 15 to 17 hours followed by rinsing with acetonitrile to remove the non-adsorbed dye and drying at 50°C for several minutes. The front electrode thereby produced was immediately used in assembling the corresponding photovoltaic cell.

ii) *Front electrodes prepared by high pressure sintering of nano-porous titanium dioxide layers:*

Coated glass electrodes with the nano titanium dioxide dispersions were first dried at 110°C for 5 minutes, then, after cooling to room temperature (25°C), a pressure of 500 bars was applied for 5 seconds. These pressure sintered coatings were then heated to 110-150°C, then immediately immersed in a 2 x 10^{-4} M solution of the Ruthenium 535 bis-TBA dye (SOLARONIX) for 15 to 17 hours followed by rinsing with acetonitrile to remove non-adsorbed dye and drying at 50°C for several minutes. The front electrode thereby produced was immediately used in assembling the corresponding photovoltaic cell.

Cell assembly

The back electrode (consisting of SnO_2:F glass (Pilkington TEC15/3) evaporated with platinum to catalyze reduction of the electrolyte) was sealed together with the front electrode with two pre-patterned layers of Surlyn®(DuPont)(2 x 7 cm^2 where in the middle 1 x 6 cm^2 had been removed) in between. This was performed at a temperature just above 100°C on a hotplate. As soon as the sealing was completed, the cell was cooled to room temperature (25°C) and electrolyte was added through holes in the counter electrode. The electrolyte used was a solution of 0.5 M LiI, 0.05 M I_2 and 0.4 M t-butylpyridine in acetonitrile and was injected into the cell

during cell assembly. The holes were then sealed with Surlyn® and a thin piece of glass. Conductive tape was attached on both long sides of the cell to collect the electricity during measurement. Measurements were performed immediately after cell assembly.

Device characterisation:

The cell was irradiated with a Steuernagel Solar Constant 575 solar simulator with a metal halide 1 AM light source. The simulator was adjusted to about 1 sunequivalent. The electricity generated was recorded with a Type 2400 SMU Keithley electrometer. The most relevant parameter for these experiments was the short circuit current (I_{sc}) which is given for the examples in Tables 1 to 4. The open circuit voltage was in all cases almost the same (0.640 to 0.680), which was also the case for the fill factor (FF) (0.5 to 0.6). Cells with lower open circuit voltages than 0.640 V or fill factors lower than 0.5 were not considered.

i) *Photovoltaic devices incorporating sintered titanium dioxide layers prepared with Dispersion 1:*

The device parameters for reference photovoltaic devices incorporating front electrodes with sintered titanium dioxide prepared with Dispersion 1 together with the sintering conditions are given in Table 1.

Table 1:

Device	TiO_2 dispersion	Heat pretreatment	Pretreatment temperature [°C]	Sintering conditions	Layer thickness (µm)	I_{sc} [mA/cm^2]
1(ref)	1	No	-	450°C	3.2	4.76
2(ref)	1	No	-	450°C	3.6	4.56
3(ref)	1	No	-	450°C	4.8	5.49
4(ref)	1	No	-	450°C	8.0	5.40
5(ref)	1	No	-	450°C	17.0	5.80
6(ref)	1	No	-	Pressure	1.4	1.32
7(ref)	1	No	-	Pressure	2.1	1.68
8(ref)	1	No	-	Pressure	2.5	2.58
9(ref)	1	No	-	Pressure	4.0	4.90
10(ref)	1	No	-	Pressure	5.5	4.37
11(ref)	1	No	-	Pressure	5.9	5.19
12(ref)	1	No	-	Pressure	9.5	4.58
13(ref)	1	No	-	Pressure	16.0	5.50

The results in Table 1 show that Devices incorporating high pressure sintered titanium dioxide layers prepared with Dispersion 1 yielded, for similar layer thicknesses, comparable short circuit currents, I_{sc}, to Devices incorporating high temperature sintered titanium dioxide layers, as to be expected from the teaching of WO 00/72373.

ii) *Photovoltaic devices incorporating sintered titanium dioxide layers prepared with Dispersions 1 and 2:*

The short circuit currents, I_{sc}, for photovoltaic devices incorporating front electrodes with sintered titanium dioxide layers prepared with Dispersion 2 are given in Table 2 together with information concerning the heat pretreatment of Dispersion 2 and the sintering conditions used. The short circuit currents, I_{sc}, device parameters for the photovoltaic devices of reference Devices 2, 8 and 9 are also included in Table 2 by way of reference.

Table 2:

Device	TiO_2 dispersion	Heat pre-treatment	Pretreatment temperature [°C]	Sintering conditions	Layer thickness (µm)	I_{sc} [mA/cm^2]
2(ref)	1	No	-	450°C	3.6	4.56
8(ref)	1	No	-	Pressure	2.5	2.58
9(ref)	1	No	-	Pressure	4.0	4.90
14(comp)	2	No	-	450°C	2.8	7.02
15(comp)	2	No	-	Pressure	3.1	0.96
16(comp)	2	Yes	450°C	450°C	2.6	6.68
17(inv)	2	Yes	450°C	Pressure	3.1	6.73

The results in Table 2 show that photovoltaic cells incorporating high temperature sintered titanium dioxide layers, as expected from the prior art, exhibited high short circuit currents, that prepared with Dispersion 2 without heat pretreatment exhibiting a much higher short circuit currents than those exhibited by photovoltaic cells incorporating high temperature sintered titanium dioxide layers prepared with Dispersion 1.

The results in Table 2 also show that for comparable titanium dioxide layer thicknesses the photovoltaic cell of Device 2 incorporating a high pressure sintered titanium dioxide layer prepared with Dispersion 1 exhibited a comparable short circuit current to that of Device 9 incorporating a high temperature

sintered titanium dioxide layer prepared with Dispersion 1, in accordance with the teaching of WO 00/72373.

However, if photovoltaic cells incorporated titanium layers prepared with Dispersion 2 without pretreatment, Device 15 incorporating a high pressure sintered layer exhibited a short circuit current which was much lower that that of Device 14 incorporating a high temperature sintered layer, at variance the teaching of WO 00/72373.

If, however, Dispersion 2 pretreated at 450°C was used, according to the present invention, instead of Dispersion 2 without pretreatment, then short circuit currents comparable with that observed with Device 14 incorporating a high temperature sintered layer of Dispersion 2 without pretreatment were observed, whether high pressure sintering was used, as in the case of Device 17, or high temperature sintering was used, as in the case of Device 16.

This demonstrates the advantage of the present invention in making it possible to realize high short circuit currents in photovoltaic devices incorporating a high temperature sintering layer of a metal oxide semiconductor nano-particle dispersion prepared by a wet precipitation process, if the dispersion is subjected to prior thermal treatment.

iii) *Influence of titanium dioxide layer thickness on photovoltaic device performance:*

Table 3 gives the results obtained with further photovoltaic devices with front electrodes prepared with Dispersion 2 for different titanium dioxide layer thicknesses, together with information regarding the heat pretreatment and sintering conditions. The short circuit currents, I_{SC}, device parameters for the photovoltaic devices of comparative Device 14 and invention device 17 are also included in Table 3 for the sake of comparison.

The results in Table 3 show that the short circuit current increased with titanium dioxide layer thickness for photovoltaic devices incorporating high pressure sintered titanium dioxide layer prepared with Dispersion 2 with heat pretreatment, according to the present invention, and moreover that the short circuit currents for photovoltaic devices with high temperature sintered titanium dioxide layers prepared with Dispersion 2 with heat pretreatment were comparable to those attained with photovoltaic devices incorporating high pressure sintered titanium dioxide layers at all titanium dioxide layer thicknesses.

Table 3:

Device	TiO_2 dispersion	Heat pretreatment	Pretreatment temperature [°C]	Sintering conditions	Layer thickness (µm)	I_{sc} [mA/cm^2]
18(comp)	2	No	-	450°C	2.6	7.24
19(comp)	2	No	-	450°C	2.7	6.83
14(comp)	2	No	-	450°C	2.8	7.02
20(comp)	2	Yes	450°C	450°C	0.9	2.45
21(comp)	2	Yes	450°C	450°C	1.0	2.51
22(comp)	2	Yes	450°C	450°C	1.5	4.21
23(comp	2	Yes	450°C	450°C	1.5	4.42
24(comp)	2	Yes	450°C	450°C	1.7	4.10
25(comp)	2	Yes	450°C	450°C	1.8	5.17
26(comp	2	Yes	450°C	450°C	2.5	6.41
16(comp)	2	Yes	450°C	450°C	2.6	6.68
27(comp)	2	Yes	450°C	450°C	2.6	7.83
28(comp)	2	Yes	450°C	450°C	3.8	7.00
29(comp)	2	Yes	450°C	450°C	4.8	7.81
30(inv)	2	Yes	450°C	Pressure	0.7	1.82
31(inv)	2	Yes	450°C	Pressure	0.8	2.00
32(inv)	2	Yes	450°C	Pressure	0.8	1.63
33(inv)	2	Yes	450°C	Pressure	1.4	4.18
34(inv)	2	Yes	450°C	Pressure	1.4	3.62
35(inv)	2	Yes	450°C	Pressure	1.5	3.75
36(inv)	2	Yes	450°C	Pressure	1.5	3.82
37(inv)	2	Yes	450°C	Pressure	2.2	4.14
38(inv)	2	Yes	450°C	Pressure	2.4	4.91
17(inv)	2	Yes	450°C	Pressure	3.1	6.73

iv) *Influence of the heat pretreatment temperature used for the titanium dioxide dispersion upon photovoltaic device performance:*

The short circuit currents, I_{sc}, for photovoltaic devices with front electrodes incorporating sintered titanium dioxide layers prepared with Dispersion 3 sintered at different pretreatment temperatures are given in Table 4 together with information concerning the heat treatment of the Dispersion and of the sintering conditions used. The short circuit currents, I_{sc}, device parameters for the photovoltaic devices of comparative Devices 14 and 15 are also included in Table 4 for the sake of comparison.

Table 4:

Device	TiO_2 dispersion	Heat pretreatment	Pretreatment temperature [°C]	Sintering conditions	Layer thickness (µm)	I_{sc} [mA/cm^2]
14(comp)	2	No	-	450°C	2.8	7.02
15(comp)	2	No	-	pressure	3.1	0.96
39(comp)	3	Yes	200	450°C	5.0	8.82
40(inv)	3	Yes	200	pressure	4.5	1.07
41(comp)	3	Yes	350	450°C	1.7	4.10
42(inv)	3	Yes	350	pressure	2.2	4.14
43(comp)	3	Yes	400	450°C	1.5	3.82
44(inv)	3	Yes	400	pressure	2.2	4.89
45(comp)	3	Yes	450	450°C	1.6	3.51
46(inv)	3	Yes	450	pressure	1.8	2.77
47(inv)	3	Yes	450	pressure	2.0	2.50
48(inv)	3	Yes	450	pressure	2.2	2.54
49(inv)	3	Yes	450	pressure	2.4	2.85

The results in Table 4 show that the short circuit current of photovoltaic devices incorporating a high pressure sintered titanium dioxide layer prepared with Dispersion 3 with heat pretreatment, according to the present invention, are comparable with the short circuit current of photovoltaic devices incorporating a high temperature sintered titanium dioxide layer prepared with Dispersion 3 with the same heat pretreatment for pretreatment temperatures of 350 and 400°C, see the results for Devices 42 and 44 versus Devices 41 and 43.

The short circuit currents of a photovoltaic devices incorporating a high pressure sintered titanium dioxide layer prepared with Dispersion 3 heat pretreated at 450°C, Devices 46-49, were slightly below that of Device 45 incorporating a titanium dioxide layer prepared with Dispersion 3 with the heat pretreatment at 450°C and sintered at 450°C.

Furthermore, the short circuit current of a photovoltaic device incorporating a high pressure sintered titanium dioxide layer prepared with Dispersion 3 with heat pretreatment at 200°C, Device 40, was significantly below the short circuit current of that of Device 39 incorporating a high temperature sintered titanium dioxide layer prepared with Dispersion 3 with heat pretreatment at 200°C.

EXAMPLE 2

Low temperature heat treatment after high pressure sintering

Photovoltaic devices were prepared as described for Device numbers 46 to 49 except that the titanium dioxide layer thicknesses were different and that after sintering the titanium dioxide layers were heated for 5 minutes at 150°C before drying. The short circuit currents obtained with these devices, Devices 50 to 52, together with details over their titanium dioxide layer thickness and processing are given in Table 5 together with the results for Devices 46 to 49.

Table 5:

Device	TiO_2 dispersion	Heat pre-treatment at 450°C	Sintering conditions	Post-pressure sintering heating temperature [°C]	Layer thickness (μm)	I_{sc} [mA/cm^2]
46(inv)	3	Yes	pressure	-	1.8	2.77
47(inv)	3	Yes	pressure	-	2.0	2.50
48(inv)	3	Yes	pressure	-	2.2	2.54
49(inv)	3	Yes	pressure	-	2.4	2.85
50(inv)	3	Yes	pressure	150	0.9	2.05
51(inv)	3	Yes	pressure	150	1.1	2.53
52(inv)	3	Yes	pressure	150	1.4	3.03

Taking into account the increase in short-circuit current with increasing titanium dioxide layer thickness, it is clear that post-pressure sintering heating at moderate temperatures increased the short-circuit current observed.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. A process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of said heat-treated nano-particles from step (ii), (iv) applying said dispersion prepared in step (iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature below 250°C.

2. Process according to claim 1, wherein said metal oxide is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

3. Process according to claim 1, wherein said pretreatment temperature is in the range of 300 to 500°C.

4. Process according to claim 1, wherein said sintering pressure is in the range 400 to 600 bar.

5. Process according to claim 1, wherein the process further comprises heating said coating subjected to pressure from step (v) at a temperature of 100 to 200°C.

6. Process according to claim 1, wherein said nano-porous metal oxide semiconductor has a band-gap of greater than 2.9 eV.

7. Process according to claim 1, wherein said nano-porous metal oxide nano-particles have a mean number averaged particle size ≤ 20 nm.

8. A layer of a nano-porous metal oxide semiconductor obtainable by a process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of said heat-treated nano-particles from step (ii),

(iv) applying said dispersion prepared in step (iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature between 20 and 250°C.

9. Layer according to claim 8, wherein said layer contains at least one spectral sensitizer for the nano-porous metal oxide semiconductor selected from the group consisting of metal chalcogenide nano-particles with a band-gap between 1.5 and 2.9 eV, organic dyes, and metallo-organic dyes.

10. A photovoltaic device comprising a layer of a nano-porous metal oxide semiconductor obtainable by a process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of said heat-treated nano-particles from step (ii), (iv) applying said dispersion prepared in step (iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature below 250°C.

ABSTRACT

PROCESS FOR PREPARING NANO-POROUS METAL OXIDE SEMICONDUCTOR LAYERS

A process for preparing a layer of a nano-porous metal oxide semiconductor comprising the steps of: (i) providing metal oxide semiconductor nano-particles prepared by a wet precipitation process, (ii) heating said nano-particles at a temperature in the range of 250 to 600°C, (iii) preparing a dispersion of said heat-treated nano-particles from step (ii), (iv) applying said dispersion prepared in step (iii) to a support to produce a coating; and (v) subjecting said coating to a pressure in the range of 100 to 1000 bar at a temperature below 250°C; a layer of a nano-porous metal oxide semiconductor obtainable by this process; and a photovoltaic device comprising a layer of a nano-porous metal oxide semiconductor obtainable by this process.